Novel Electrochemistry of The Ru(0001) Surface Towards Electrocatalysis At Molecular Level

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Abstract

Ex-situ LEED, RHEED and Auger data have shown that the Ru(0001) electrode shows the potential-dependent formation of well-defined and ordered oxygen-containing adlayers of (2x2), (3 x 1) and (1 x 1)-O and finally RuO_2(100) islands in perchloric acid solution. The adsorption and electro-oxidation of methanol, formic acid and CO at the Ru(0001) electrode have been investigated as a function of temperature, potential and time using *in-situ* FTIR spectroscopy, and the results interpreted in terms of the surface chemistry of the Ru(0001) electrode. It was found that the oxide phases have a marked effect upon the reactivity of the surface towards the electro-oxidation of such fuel molecules; in addition, it is clear from the data that RuO_2 is significantly active towards the oxidation of both methanol and formic acid.

It was found that no dissociative adsorption or electro-oxidation of methanol takes place at the Ru(0001) at potentials < 800 mV vs Ag/AgCl, and at all three temperatures employed, 10 °C, 25 °C and 50 °C. However, formic acid did undergo dissociative adsorption, even at -200 mV, to form linearly adsorbed CO, (CO_L), with little or no CO adsorbed at threefold-hollow sites, (CO_H). In contrast to the adsorption of CO, it was found that increasing the temperature to 50 °C markedly increased the amount of CO_L formed on the Ru(0001) surface from the adsorption of formic acid. On increasing the potential, the electro-oxidation of the CO_L species to CO_2 took place *via* reaction with the active (3 x 1)-O oxide. At all three temperatures employed, it was found that the formic acid was oxidised to CO_2 faster than was observed in the experiments involving CO adsorbed from CO(g) over the potential range at which oxidation of CO_L was observed, suggesting a higher mobility of the CO_L species formed from the adsorption of the HCOOH. At potentials > 1000 mV, the oxidation of formic acid to CO_2 was significantly increased, and the oxidation of methanol to CO_2 and methyl formate was observed, both of which were attributed to the formation of an active RuO_2 phase on the Ru(0001) surface.